



Estimation of the heat generation rates in electrochemical cells



Henry A. Catherino

Electrical and Computer Engineering Department, Oakland University, Rochester, MI 48063, USA

HIGHLIGHTS

- The heat generation rate for single cells and multi-cell batteries is estimated.
- The heat generation rate during cell venting is estimated.
- The heat generation rate is estimated without requiring a temperature measurement.
- The thermal response of a battery is a measure of its state of health.
- A simple first order differential equation models the dynamic thermal response.

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ABSTRACT

One of the earliest attempts to estimate the heat production rate in an electrochemical cell is that of Sherfrey and Brunner [1]. Their methodology and the developments that followed generated models of greater or lesser sophistication that are difficult to apply because of notation problems. In many cases, the modeling equations are referenced in subsequent papers but the cell's thermal response continues to be determined experimentally. A computationally simpler approach is developed and evaluated. This methodology follows essentially the original methodology but begins at a more fundamental level, i.e., the energy conservation law. By doing this, the critical parameters are easily addressed in a more systematic way and produce quantitative results suitable for more extended modeling and simulation exercises. These quantitative parameters include (1) the heat generation rate in multi-cell batteries, (2) the heat generation rate during cell venting, (3) the thermal response as a measure of the state of health of a battery, (4) an estimator of the heat generation rate that does not require a temperature measurement and (5) a first order differential equation that models the dynamic thermal response as a function of the power input (or output) of the battery.

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1. Introduction

The objective of this effort is to develop a method for estimating the rate of heat generation in an electrochemical cell during charge and discharge. It is understood that this objective has been the focus of a number of earlier studies. The early paper that is most often referenced as the starting point for estimating the thermal response of electrochemical cells is that of Sherfrey and Brunner [1].

The methodology presented there is to break the heat generation rate into a reversible and an irreversible part. The reversible heat component is associated with the Entropic changes taking place in the cell as current passes and the electrochemical reaction proceeds. The irreversible part is the contribution of Joule heating resulting from the fixed resistive components within the cell and

the consequence of the polarization at each of the cell electrodes. Basically,

$$Q_{\text{cell}} = Q_{\text{Entropic}} + Q_{\text{Joule}} + Q_{\text{Electrode Polarization}} \quad (1)$$

The studies that followed focused on determining the power components associated with each of these parts. A sampling of applications of this methodology appears in the following references [2–8].

As a practical matter, the developed models used to estimate the heat generation rate are mathematically barely tractable. There also appears to be a tendency only to reference the modeling equations and then the sought after heat generation data is measured experimentally. In this study, a methodology is being sought to allow for a more convenient way to estimate the thermal response of electrochemical cells.

As a point of clarification, the polarization resistance used in the text that follows includes the summation of all of the resistances. The polarization resistance is determined as the difference between

E-mail address: henry.catherino@comcast.net.

Nomenclature

A	area (m^2)
C_p	heat capacity ($\text{J}^\circ\text{C}^{-1}$)
E	cell or battery voltage (V)
E_{EQ}	equilibrium voltage (V)
F	Faraday
h	heat transfer coefficient ($\text{W m}^{-2} \text{ }^\circ\text{C}^{-1}$)
I	current (A)
m	number of cells wired in series
n	number of equivalents per mole
n^*	number of moles
P	pressure (Atm)
Q_{battery}	rate of heat generation in a battery (W)
Q_{cell}	rate of heat generation in a cell (W)
$Q_{\text{ElectrodePolarization}}$	rate of heat generation associated with electrode polarization (W)

Q_{Entropic}	rate of heat generation of absorption associated with Entropic changes (W)
$Q_{\text{irreversible}}$	rate of irreversible heat generation (W)
$Q_{\text{Polarization}}$	rate of heat generation associated with cell polarization (W)
Q_{Joule}	rate of heat generation from resistive components (W)
$Q_{\text{reversible}}$	rate of reversible heat generation (W)
R	the gas constant ($\text{LAtm mol}^{-1} \text{ K}^{-1}$)
T	cell temperature ($^\circ\text{C}$)
T_a	ambient temperature ($^\circ\text{C}$)
T^*	absolute temperature (K)
V	volume (L)
ΔG	Gibbs Free Energy of Reaction (J mol^{-1})
ΔH	Enthalpy of Reaction (J mol^{-1})
ΔS	Enthalpy of Reaction (J mol^{-1})

the equilibrium voltage (at zero applied current) and the voltage measured at any specific applied current. So, in the discussion that follows

$$Q_{\text{cell}} = Q_{\text{Entropic}} + Q_{\text{Polarization}} \quad (2)$$

and so for the net polarization

$$Q_{\text{polarization}} = Q_{\text{Joule}} + Q_{\text{Electrode Polarization}} \quad (3)$$

The Entropic term refers to the heat generated by virtue of the structural changes taking place in the transition from reactants to products resulting from the electrochemical reaction taking place in the cell. This transition involves the energy changes associated with the changes in the Entropy between the reactants and the products. Since this quantity is independent of how fast the reaction takes place (it depends only on the initial and final states), it is the reversible part of the heat generated in the reaction.

$$Q_{\text{cell}} = Q_{\text{reversible}} + Q_{\text{irreversible}} \quad (4)$$

In the text that follows, the Joule heating effect is understood to include the entire heating consequence of current passing through all of the resistances in the cell including the resistance associated with the electrode polarizations. Although the discussion that follows addresses battery systems, it is to be understood that the analysis can apply to electrochemical cells generally.

2. Method

The methodology developed here basically takes a slightly different tack on the estimation of the heat generation. Rather than attempt to determine the heat generation rate directly, the approach is to back it out of the conservation laws. It is worthy of note, this methodology gives no information about the mechanistic descriptions that are dealt within substantial detail in the cited references. The energy conservation law requires that

$$C_p \frac{dT}{dt} + hA(T - T_a) + \frac{I}{nF} \Delta H = EI \quad (5)$$

Many of the terms from this equation are well known but in some of the terms there are some tricky details that are easily overlooked. The first term on the left is the power involved in heating the thermal mass of the cell. The heat capacity at constant pressure (C_p) of the cell is the summation of the specific heat–mass product of the individual cell components. This term also identifies

the equation as a first order differential equation for the rate of temperature (T) change with respect to time. The second term on the left is the power lost to (or gained from) the environment by the cell across a thermal gradient. The term, hA , is the heat transfer coefficient (h) multiplied by the area (A) of the mass undergoing the heat transfer. It is critical to note that h is not the convective heat transfer coefficient. It is unfortunate that the same symbol is used in textbooks to represent both quantities without sufficient explanation. In this case, h , includes the power contributions of conduction, convection and radiative heat transfer. Although the radiative component is known to occur across a thermal gradient of absolute temperatures where the temperatures are raised to the fourth power, it can be shown that in the ranges of temperature normally experienced by batteries, the usual temperature gradient as shown in Equation (5) is an excellent approximation. As a point of explanation, this approximation applies whenever the absolute temperature of the cell is approximately equal to the absolute temperature of the environment. The third term on the left hand side is the power involved in driving the chemical reaction in the battery. It is normally the case that this is a single process so that the Enthalpy term is that of the energy storage reaction in the battery. Perhaps a better way of stating this is to say that, in this case, a single chemical process is the major and predominating contributor to the observed Enthalpy of Reaction during the charging and discharging of the cell. One measure of the fidelity of this approximation is the current efficiency of the reaction. F , is the Faraday and n is the number of moles of electrons produced per mole of reactant involved in the reaction. Or more precisely, n is the number of equivalents per mole of reactant. The Enthalpy of Reaction is understood to be a one dimensional vector quantity so as to signify that its sign changes depending on the direction of the reaction. By convention, its magnitude is given a negative sign whenever the thermodynamic system under consideration loses energy and positive when it gains energy. The Enthalpy of Reaction is not to be confused with the Heat of Reaction. The former is a vector whereas the latter is a scalar. The absolute value of the Enthalpy of Reaction equals the Heat of Reaction. The current, I , can also become a problem here. Current is normally considered a scalar quantity. However, in the application of Kirchhoff's Laws as applied in circuit analysis, the current is given a positive or negative value depending on its direction. This makes the current magnitude appear to have a vector-like property. What complicates this is that the selection of the initial reference direction is arbitrary. That is, the direction of the positive current is arbitrarily selected and once it has been selected, the negative current is then established as

flowing in the opposite direction. This can lead into some interesting sign selection problems. Returning to the equation under discussion, the term on the right hand side is the power delivered to or taken away from the cell. In this case, E is the voltage across the cell and I is the current passing through the cell. This is a second instance where the issue of the consistency of sign selection could become a problem.

For the sake of clarity and simplicity, the current shall be understood to be a scalar quantity given always as a positive value in the text that follows. By doing that, Equation (5) becomes the energy balance during the charging of the cell with the understanding that the value of ΔH is a positive quantity.

In like manner, the discharge of the cell can be written as:

$$-\frac{I}{nF}\Delta H = Cp\frac{dT}{dt} + hA(T - Ta) + EI \quad (6)$$

This form of the equation serves to emphasize that the chemical reaction is the power source that distributes the generated power over the components shown on the right hand side of the equation. Note that in the discharge, the Enthalpy of Reaction is a negative quantity. Again, current is taken as a positive quantity. One can make the immediate observation that if one carefully defines the current in terms of a positive and negative flow so as to distinguish a charge and a discharge, the two equations are actually the same. In the discussion that follows, there will be an adherence to the positive sign given to the current during both charge and discharge so that two separate equations are required. This equation states that the power generated by the chemical reaction in the cell is distributed so as (1) to store the power in the thermal mass of the cell, (2) to transfer to or receive power (heat) between the environment and the cell and (3) to deliver power to a load. The consequence of this is that during charge

$$Q_{\text{cell}} = Cp\frac{dT}{dt} + hA(T - Ta) = -\frac{I}{nF}\Delta H + EI \quad (7)$$

and during discharge

$$Q_{\text{cell}} = Cp\frac{dT}{dt} + hA(T - Ta) = -\frac{I}{nF}\Delta H - EI \quad (8)$$

We have here a lumped constant method for estimating the total heat generated in an electrochemical cell which is simple and direct. In addition, solving the differential equation allows the temperature of the cell to be predicted for any applied power profile. The next step is to validate these claims experimentally.

There is one more observation that is curious. Using this conservation law statement, and the definition of Enthalpy in terms of the Entropy and Gibbs Free Energy, one can derive the relationship given in the Sherfery and Brunner paper. That is, if one then uses the relationship between the Free Energy and the equilibrium voltage:

$$\Delta G = -nFE_{EQ} \quad (9)$$

the polarization term can then be defined. That is, we can take the equation for the discharge reaction (3) and solve it for the heat generation rate in the cell. The Enthalpy term is replaced by its equivalent as the Entropy and Gibbs Free Energy.

$$\Delta H = \Delta G + T\Delta S \quad (10)$$

The Gibbs Free Energy is replaced by its equivalent in terms of the equilibrium voltage and the Entropy term is replaced by its equivalent which is:

$$\Delta S = nF\frac{dE_{EQ}}{dT} \quad (11)$$

Then the well-established heat generation rate equation is derived.

$$Q_{\text{cell}} = -IT\frac{dE_{EQ}}{dT} + I(E_{EQ} - E) \quad (12)$$

What is curious is that the measured equilibrium voltage does not change sign with the direction of the reaction whereas the thermodynamically derived equilibrium voltage changes sign with the direction of the reaction. The polarization, η , is the difference between the measured cell voltage and the thermodynamically established equilibrium voltage. Since the former does not change sign with current reversal but the latter does, then this suggests that the attempt at validating the equations appearing in the literature can be very tricky in order to be used in actual modeling. It is worthy of note that the theoretical descriptions found in the literature appear to omit mentioning this detail. It may be that the original authors consider this an obvious point not requiring further mention. As a consequence, casual users who attempt to apply these equations are left with the need to arbitrarily change the signs of the terms in order to make the equation conform with the measurements. Doing this does not instill very much confidence in the validity of the theoretical analyses by casual users. A more complete explanation of this situation is presented in the appendix to this paper.

3. Experimental

To demonstrate the applicability of this approach, measurements were made on cells of different chemistries. The study that follows uses a small VRLA cell as the object of interest. This same study was also performed on nickel cadmium and nickel metal hydride cells.

A cell was prepared for measuring the current, voltage and surface temperature. The temperature was measured using an attached thermocouple. Digital voltmeters having at least a 10 M Ω input impedance were used to make the voltage measurements. The current was measured within an uncertainty of ± 1 mA and the temperature measurement used a type K thermocouple that measured the temperature with a resolution of ± 0.1 °C and a measured stability of ± 0.25 °C. The cell was standing on a table top and the natural convective heat transfer condition existed driven by the ambient room temperature environment. The chatter in the data was the consequence of the limited data resolution of the data acquisition system used in sampling and recording the data. The oscillatory appearance of the temperature data is consistent with the ambient temperature regulation.

Three regions are identified in Figs. 1 and 2. Basically, a fully discharged cell was charged at constant current, allowed to go into overcharge until a steady state temperature was achieved and then the current was turned off allowing the cell to cool down. The current was maintained at a low enough level to ensure that the cell did not vent in overcharge. Maintaining a closed oxygen cycle is critical in the analysis that follows. A discussion of the effect and consequences of cell venting appears later in this paper. For the sake of clarity, there are a number of ways to ensure that the cell is not venting during a constant current overcharge. The author's preferred method was to measure the cell temperature as a function of applied power. This response is linear up to the point where venting takes place. At that point the temperature begins to deviate below the linear response extrapolation. The venting action results in an observable cooling of the cell. The vent free measurements were made at a current level in the linear part of the curve and at a

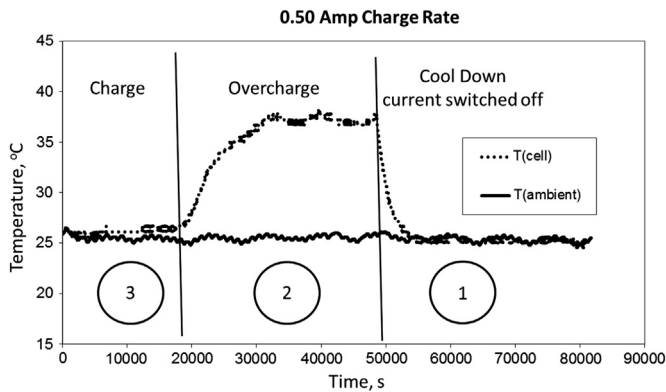


Fig. 1. The temperature–time charging curve for a sealed lead acid cell in a wound configuration rated at 2.5 Ah.

current level sufficient to achieve a good measurement of the difference between the cell and the ambient temperatures.

The first region identified by the number 1 shown in Fig. 1 is the cooling curve where the cell is dissipating its thermal energy into the environment. The data from the cooling curve is addressed using Newton's Law of Cooling. Specifically,

$$q = hA(T - T_a) \quad (13)$$

and

$$q = C_p \left(\frac{dT}{dt} \right) \quad (14)$$

where q is the rate of heat generation or absorption. It is worth reiterating a point made earlier that in applying Newton's Law of Cooling, the symbol, h , includes the conductive, convective and radiative components of heat transfer. Further, in this case it is not necessary to distinguish the heat transfer coefficient from the area term. The product, hA , will be carried as a composite term in the analysis that follows. So,

$$\frac{dT}{dt} = \frac{hA}{C_p}(T - T_a) \quad (15)$$

giving

$$\ln \left(\frac{T - T_a}{T_0 - T_a} \right) = -\frac{hA}{C_p} t \quad (16)$$

where T_0 is the temperature selected to represent the beginning of the cool down. The slope of the logarithmic term against time

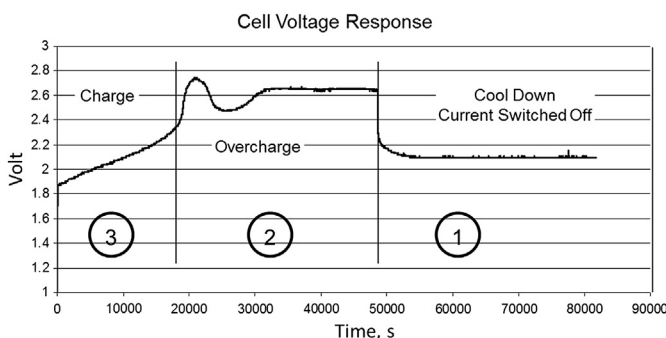


Fig. 2. The voltage–time charging curve for a sealed lead acid cell in a wound configuration rated at 2.5 Ah.

is, $-hA/C_p$. To determine the discrete values of hA and C_p , an examination of region 2 permits the achievement of this objective.

In region 2, the cell is in overcharge and a thermal steady state has been achieved. Looking again at Equation (5), the derivative term is zero and since the battery is fully charged and only the closed oxygen cycle is active, the Enthalpy of Reaction term is also equal to zero. The latter observation might need further explanation [9]. Simply put, the Enthalpy of Reaction for all closed chemical cycles is exactly zero. This is a requirement of the Energy Conservation Law. It is also known as Hess' Law.

This leaves the expression which simply states that the power input to the cell is equal to the power dissipated into the environment.

$$hA(T - T_a) = EI \quad (17)$$

From the measured temperature gradient and the measured power delivered to the cell, the product, hA , is established. Knowing the value of hA from region 2 and the slope, $-hA/C_p$, from region 1, the value of C_p is established. C_p for this cell was 169 J K^{-1} and hA was 0.111 W K^{-1} . Having done this, all that remains is to estimate the value of the Enthalpy of Reaction for the cell.

Rearranging Equation (5) and solving for the Enthalpy term gives

$$\Delta H = \frac{nF}{I} \left(EI - hA(T - T_a) - C_p \frac{dT}{dt} \right) \quad (18)$$

The derivative term is virtually zero which is evident from the data shown in region 3 of Fig. 1. This is the case because such a small cell was used. In larger cells, the effect of the gradual temperature change of the mass of the cell could be estimated from the data. In this manner, the Enthalpy of Reaction can be plotted as a function of time during the entire charging event.

For comparison purposes, the Standard Enthalpy of Reaction for the Lead Acid reaction has been established in the literature as $359.4 \text{ kJ mol}^{-1}$. Fig. 3 shows a slight increasing trend in the data. This is to be expected as the sulfuric acid concentration in the electrolyte is changing by virtue of its being one of the reaction products being generated during the charging process. The decreasing enthalpy at the end of the charging process is the consequence of the transition to overcharge where the Enthalpy of Reaction is zero for the closed oxygen cycle.

At this point, all of the constants are in hand for estimating the thermal response of this chemistry. The dynamic response of the cell temperature can be simulated by solving the differential equation given by Equation (5).

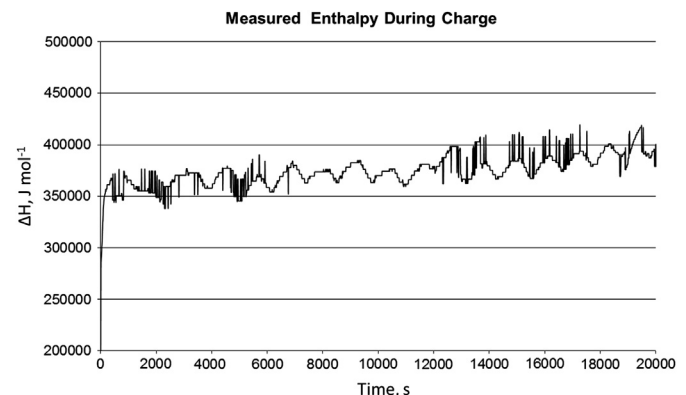


Fig. 3. The Enthalpy of Reaction for the lead acid chemistry is plotted from data taken during the charging of the cell.

Equation (7) provides an interesting alternative path for estimating the heat generated in a cell. Ordinarily, the heat generated in a cell can be determined by monitoring the cell temperature as

$$Q_{\text{cell}} = Cp \frac{dT}{dt} + hA(T - T_a) \quad (19)$$

This can sometimes be a source of problems especially when the temperature measurement contains a large uncertainty. By having to subtract two numbers having a large inherent error makes the difference even more uncertain. However, Equation (7) also shows that

$$Q_{\text{cell}} = -\frac{I}{nF} \Delta H + EI \quad (20)$$

In this case, the heat generation rate in the cell is determined by the current passing through the cell, the voltage across it and the Enthalpy of Reaction. All of these are easily determined and gives a much better estimate of the heat generation rate. This equation states that during the charging process, power input into the cell minus the power absorbed to drive the chemical reaction leaves the remaining power that acts to raise (or lower) the temperature of the cell. The heat generation response is shown in Fig. 4.

The discussion thus far has focused on the charging process. This analysis was also performed on nickel metal hydride and nickel cadmium cells. For the nickel metal hydride cell, the Enthalpy of Reaction was measured as 240 kJ mol^{-1} and that for the nickel cadmium cell was measured as 270 kJ mol^{-1} .

Similarly, the discharge of the cell was analyzed using Equation (6). A fully charged cell was discharged through a fixed resistor having a measured value of 2.77 Ohms . The characteristic constants for Cp and hA were determined earlier. Fig. 5 shows the calculated values for the Enthalpy of Reaction.

This data is in agreement with that determined from the charging data. The plot of the internal heat generated during the discharge under these experimental conditions shows a very small mixed effect as seen in Fig. 6

That is, the analysis suggests an endothermic response early in the discharge that becomes exothermic during the end of the discharge. Although the thermal effect is very small, the effect would be the result of the competition between the chemical reaction driving the load and at the same time extracting heat from or liberating heat to the environment to drive the reaction.

3.1. Cell venting comment

The determination of the heat transfer coefficient–area product term required that the cell did not vent. The physical model existing

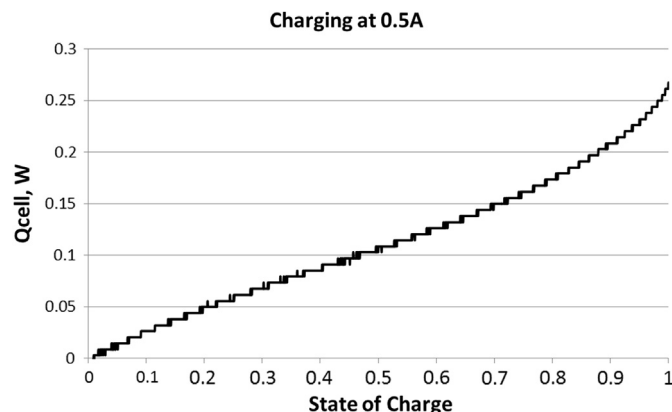


Fig. 4. Heat generation in a sealed lead acid cell using Equation (20).

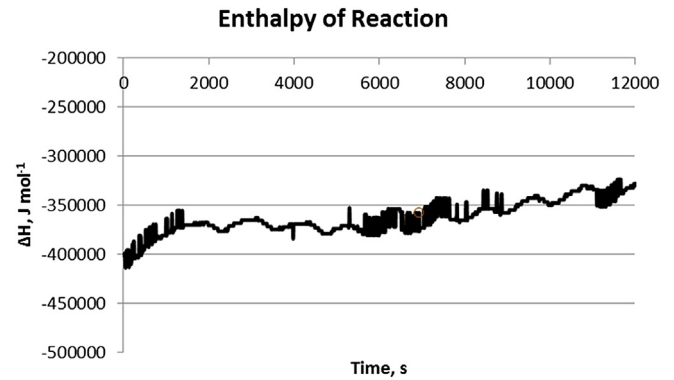


Fig. 5. The reaction Enthalpy on discharge calculated from the modeling equation.

under these conditions is an interesting one. A common sense observation might be that the vented gases remove heat from the cell. This is easily discounted as the amount of gas vented has such low heat capacities that this contribution is of no significance. A model that makes more sense is that the additional cooling effect is attributable to the electrolysis of water. The Standard Enthalpy of Reaction for this process is $+285.8 \text{ kJ mol}^{-1}$. The energetic reaction products (hydrogen and oxygen) exit the cell and recombine somewhere else in the universe. There the stored energy is recovered by the oxidation of the hydrogen by oxygen. The point is that this energy recovery does not take place in the cell but rather, in another place far from it.

What follows is an attempt to estimate the cooling effect resulting from the electrolysis of the solvent which is determined from the gas evolution rate exiting the cell. The venting process is visualized as the consequence of the reaction:



Then

$$\frac{3}{2} \left(\frac{dn^*(\text{water})}{dt} \right) = \frac{dn^*(\text{gas})}{dt} \quad (22)$$

In this case, n^* signifies the number of moles. The perfect gas equation:

$$PV = n^*RT^* \quad (23)$$

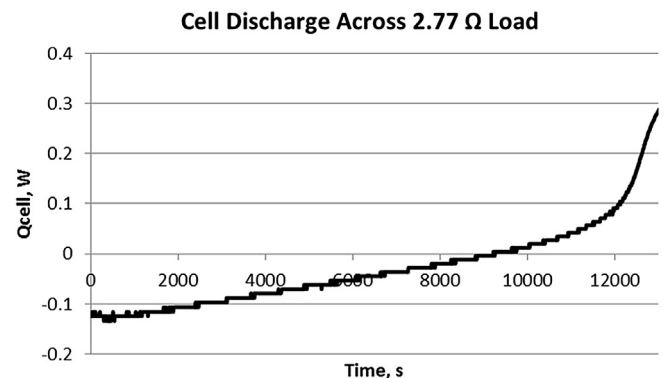


Fig. 6. Plot of the calculated heat generation during the cell discharge using the modeling equation.

where T^* is the absolute temperature, shall be used to make the prediction. Taking the partial derivative with respect to time and rearranging,

$$\frac{\partial n^*(\text{gas})}{\partial t} = \frac{P}{RT^*} \frac{\partial V}{\partial t} \quad (24)$$

then

$$\frac{\partial V}{\partial t} = \left(\frac{RT^*}{P} \right) \frac{\partial n^*(\text{gas})}{\partial t} \quad (25)$$

and solved for the rate of water loss associated with the rate of gas production rate gives

$$\frac{\partial V}{\partial t} = 1.5 \left(\frac{RT^*}{P} \right) \frac{\partial n^*(\text{water})}{\partial t} \quad (26)$$

Going back to Equation (5) for the charging of the cell and viewing it as the governing relationship taking place during the venting of the cell, the closed cycle process generates no heat but the electrolysis is endothermic and its contribution to the overall heating effect is quantitatively given by:

$$Cp \frac{dT}{dt} + hA(T - Ta) + \frac{2}{3}(\Delta H) \left(\frac{P}{RT^*} \right) \frac{\partial V}{\partial t} = EI \quad (27)$$

where $\partial V/\partial t$ is the gassing rate and T is the temperature. Note that T^* refers specifically to the absolute temperature. Also, during overcharge, the temperature usually achieves a steady state and in that case, the heat capacity term disappears. The other terms have been defined in our previous discussions and are constants. There exists a quantitative correlation between the measured parameters. That is, by measuring the rate of gas evolution from the cell, the heat generation can be estimated for a venting cell.

The preceding discussion claims a complete (lumped parameter) interpretation of the observed heating of sealed cells during overcharge in aqueous systems (up to the boiling of the electrolyte). As exceptions have a way of falsifying absolute statements of this kind, in the case of Li-ion cells, a greater complexity exists because there is an added contribution of the exothermic decomposition of the cell materials whenever the cell temperature exceeds a well-studied threshold value [10–12].

3.2. State of health estimation comment

An interesting speculative observation comes from the examination of Equation (8) that specifies the heat generated within a cell during discharge. Only two collective terms are required. The first is the product of the Enthalpy of Reaction and the current and the second is the power delivered to the load. The Enthalpy–current product is a measure of the power produced by the chemical reaction. The difference between the power generated by the reaction and the power delivered to the load is the heat that is dissipated in the cell. In many applications, the load operates at constant power. The voltage across the load is determined by both the load resistance and the polarization resistance (i.e., the equivalent series resistance) of the cell.

In Fig. 7, a voltage division is determined by the value of the resistances shown. As a cell ages, the polarization resistance (R_p) increases and in some analytical approaches to the estimation of cell aging, this increased resistance has been used as an estimator of the state of health of the cell. This means that a cell delivering constant power to a load will have a reduced voltage applied to the load as the internal resistance of the cell increases with age. The

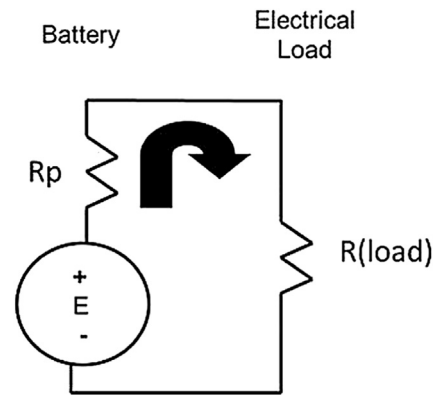


Fig. 7. Schematic of a power supply delivering a current to a resistive load.

corresponding increase in current required to maintain the constant power requirement causes the Enthalpy–current product term to increase. As a consequence, the chemical reaction generates more power in order that the load continues to operate at constant power. This means that the additional power must be dissipated within the cell. If one maintains the heat transfer environment, the cell has to operate at a higher temperature to dissipate the increased heat load. This temperature increase becomes a measure of the increase in the internal resistance of the cell and as a consequence, a measure of the state of health of the cell.

To take this one step further, if a heat exchanger is designed for this cell with a capability of holding the temperature of the cell constant, the thermal load carried by the heat exchanger becomes a measure of the state of health of the cell.

This leads to the general observation that the increased heat generation rate of an electrochemical cell relative to its initial heat generation rate at any particular delivered power to a load becomes a measure of the state of health of the cell.

It is to be noted that the point of this discussion applies equally to a battery configured as a multiplicity of cells.

3.3. High voltage battery comment

First, the equation for the thermal response of the cell also applies to multi-cell batteries. In that case, the voltage across the battery is the sum of the voltages of the single cells that are wired in series. The equation describing the thermal response requires a small modification in order to recognize the power delivered by the reaction is multiplied by the number of cells wired in series. That is, during the charging of the battery:

$$Cp \frac{dT}{dt} + hA(T - Ta) + \frac{mI}{nF} \Delta H = EI \quad (28)$$

and during the discharge:

$$-\frac{mI}{nF} \Delta H = Cp \frac{dT}{dt} + hA(T - Ta) + EI \quad (29)$$

where the value of m is the number of cells wired in series and E is the battery voltage.

Second, this method of analysis is applicable to lithium-ion chemistries as well. As a note of caution, the method for determining hA required that the cell be placed in an overcharge condition. In the author's observations, this appears to be possible if done with care. The lithium-ion cell appears to be recombinant but there is the obvious danger of putting the system into a catastrophic thermal runaway. Further, the apparent recombinant

condition resulted in a severe deformation of the cell due to a pressure build up. However, the cell did not vent and it appeared to continue cycling in a reasonably reliable manner. Had the cell vented, the usual response is a quick loss of capacity on subsequent cycling. There is a theoretical problem here in that the chemistry of any postulated recombination cycle is unknown and the appearance of what appears to be a recombinant condition does not establish that one actually exists.

Lastly, an estimator of the heat generation rate for a multi-cell battery is available. By, extending Equations (7) and (8), the battery heat generation rate in Watts during charging is:

$$Q_{\text{battery}} = -\frac{mI}{nF}\Delta H + EI \quad (30)$$

and then for the discharge:

$$Q_{\text{battery}} = -\frac{mI}{nF}\Delta H - EI \quad (31)$$

As a reminder, the Enthalpy of reaction changes sign when the direction of the reaction changes and the current is always taken to have a positive value. In the analysis presented above, the thermal properties of a cell were presented as a lumped constant. However, tools exist for modeling the thermal distribution existing in complex battery configurations. Finite element simulations of battery structures are available for analyzing both the internal heat distributions as well as the heat removal alternatives for maximum packaging efficiency [13]. Modeling of this kind requires user input of the battery's geometry, cell properties, boundary conditions and heating rate. The first three items are defined by the physical construction of the battery. The heating rate determined by the power input to or power output from the battery is established by Equations (30) and (31).

3.4. Current efficiency comment

It was mentioned earlier in the text that the analysis presumes that a single electrochemical process predominates the energetics of the process. For the most part, this is usually a good approximation. However, it is known that most electrochemical energy storage systems operate under conditions of thermodynamic instability. Specifically, the reaction between the energetic materials and the solvent are very often thermodynamically spontaneous. If it were not for the slow kinetics of these spontaneous processes, these energy storage objectives would be impossible. This implies that secondary processes occur at very low rates that appear as alternative current paths during the battery operation. The analysis presented above specifically ignores those effects. Under the test conditions of the experimental study, this approximation was a good one. Should the analysis be applied to large battery systems that may be operating at higher temperatures, the current efficiency during the battery cycle should decrease as the consequence of the thermally induced catalysis of these slow kinetic processes. In the case of the lead acid battery, the onset of gassing increases with increasing temperature. When gas evolution is recombinant, the Enthalpy of that reaction is zero which means that a larger portion of the charging power input will appear as heat. As in this example, the secondary process can contribute at a level that sufficiently large so as to require the inclusion of the secondary process into the predictive equations for the thermal response of the system.

4. Conclusion

A methodology was proposed for predicting the thermal response of electrochemical cells. The general approach is similar to

those already appearing in the literature. However, the approach begins with the energy conservation law and develops an alternative approach for calculating the thermal response of an electrochemical cell. Doing this simplifies the calculation methodology and, also, offers an algorithm that can be applied for the purposes of system control. That is, the methodology allows for quantitative estimation of (1) the heat generation rate in multi cell batteries, (2) the heat generation rate during cell venting, (3) the thermal response as a measure of the state of health of a battery, (4) an estimator of the heat generation rate that does not require a temperature measurement and (5) a first order differential equation that models the thermal response as a function of the power input (or output) of the battery.

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Appendix

We can take the Equation (6) for the thermal response of the discharge reaction and solve it for the heat generation rate in the cell. The Enthalpy term is replaced by its equivalent as the Entropy and Gibbs Free Energy.

$$\Delta H = \Delta G + T\Delta S \quad (32)$$

The Gibbs Free Energy is replaced its equivalent in terms of the equilibrium voltage.

$$\Delta G = -nFE_{EQ} \quad (33)$$

and the Entropy term is replaced by its equivalent:

$$\Delta S = nF \frac{dE_{EQ}}{dT} \quad (34)$$

Then the well-established heat generation rate equation is derived.

$$Q_{\text{cell}} = -IT \frac{dE_{EQ}}{dT} + I(E_{EQ} - E) \quad (35)$$

This appears totally consistent with that which appears in the literature.

However, a problem appears when attempting to use the cell charging Equation (5). Doing the same derivation gives the following result.

$$Q_{\text{cell}} = -IT \frac{dE_{EQ}}{dT} + I(E + E_{EQ}) \quad (36)$$

The last term on the right hand side is not a polarization term but rather a summation of the measured voltage and the equilibrium voltage. This is a very curious result.

Looking at this curiosity a little more closely and viewing it so as to make a distinction between scalar and vector quantities, the above definitions appear in a different light.

$$\Delta \vec{H} = \Delta \vec{G} + T\Delta \vec{S} \quad (37)$$

$$\Delta \vec{G} = -nF\vec{E}_{EQ} \quad (38)$$

$$\Delta \vec{S} = nF \frac{d\vec{E}_{EQ}}{dT} \quad (39)$$

An important distinction has to be made here. It is to be understood that a vector is defined as a quantity that has a magnitude and a direction. A scalar has only a magnitude with no other information attached. In this case, this definition is being adhered to for computational purposes. It is understood that one can argue that the origin of the physical quantity could define the quantity as a scalar such as current or voltage. However, the user can assign additional information to that quantity so as to create a vector quantity such as is done in the application of Kirchhoff's Laws to circuit analysis computations.

With this distinction in mind, the charging process can be reconsidered. During the charging, the Gibbs Free Energy has a positive value which means that the equilibrium voltage is actually a negative quantity. So the equation that appeared to be in the wrong form is in fact a polarization which is actually what was originally intended. This can be shown by resorting to vector notation such that

$$Q_{\text{cell}} = -IT \frac{d|\vec{E}_{EQ}|}{dT} + I(E + |\vec{E}_{EQ}|) \quad (40)$$

then

$$|\vec{E}_{EQ}| = -E_{EQ} \quad (41)$$

In this equation, the magnitude of the vector is used in place of the vector in order to add the one dimensional vector to the scalar. So the equation works just as Sherfey and Brunner envisioned it. But the user has to be very careful. The derivative term is also affected as it also changes sign.

This is now in agreement with the equations in the literature. Viewing the issue in this manner is much better than arbitrarily changing the plus sign to a minus so that the equation will conform to the experimental measurements.

It is also interesting that if the user adds-in an attempt to introduce a change in the current direction to distinguish a charging from a discharging current, the sign handling becomes a real challenge and one gets the feeling that the sign manipulations appear to be arbitrary. The difficulty lies in the fact that as the reaction is reversed, the measured voltage does not change sign and the thermodynamic voltage does change sign.

In summary, it should be clear that the measured voltage and the thermodynamically established voltage are actually different things. They are related in that the absolute value of the thermodynamically established voltage is equal to the measured voltage under the same standard and reference states.

This discussion serves to point out a conceptual problem that is carefully disguised in elementary textbooks. It does require a revisit using more powerful mathematical tools.

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